	APPROVE	ED FOR RELEASE: 06/2	3/11: CIA-RDP86-00513R000204800014-6
		<u>L 13345-61</u>	(1)/SPF(8)/MPT(m)/BDS Pb-L/Pp-L BM/MF
S:		ACCESSION NR: AF30027	7 \$/020k/63/003/003/0376/0380
7		AUTHOR: <u>Byłkovchanko</u>	V. G. J. Beresin, I. V.
c		TITLE: Investigation of cyclododecof cyclododecyl hydrope	the kinetics and mechanism of the liquid phase
			r. 3, no. 3, 1963, 376-380
		TOPIC TAGA: cyclododec cyclododecyl hydroperco	A hydroperoxide, cyclododecane, alpha-naphthol de decomposition
5		cyclododecane. Oyclodo of cyclododecane. When of cyclododecane, When of cyclododecane, or cyclodoto only product of cyclotic	dedicated to the study of the kinetics of the idecyl hydroperoxide in the process of oxidation of secyl hydroperoxide is the main product of oxidation cyclododecane is subjected to 1500 in the presence 40 minutes, the peroxide reaction is practically the n. The main oxidation products are formed by means n. The activation energy and the dependence of the
, (d)		Card 1/2	

APPROVED FOR RELEASE: 06/23/11: CIA-RDP86-00513R000204800014-6

BEREZIN, I.V.; 60 CHU [Kuo Ch'u]

Study of elementary reactions involved in the detachment of a tritium atom from pentatriacontane 18t by free cyclohexyl and heptyl radicals in the liquid phase. Dokl. AN SSSR 142 no.2:383-386 Ja '62. (MIRA 15:2)

1. Meakovskiy gosudarstvennyy universitet im. M.V.Lomonosova. Predstavleno akademikom N.N.Semenovym. (Pentatriacontane) (Tritium) (Radicals(Chemistry))

The influence of structure ...

S/020/62/144/002/022/028 B101/B110

N. Y., 1954, p. 500.

ASSOCIATION:

Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

PRESENTED:

December 26, 1961, by N. N. Semenov, Academician

SUBMITTED:

December 26, 1961

Card 3/3

The influence of structure ...

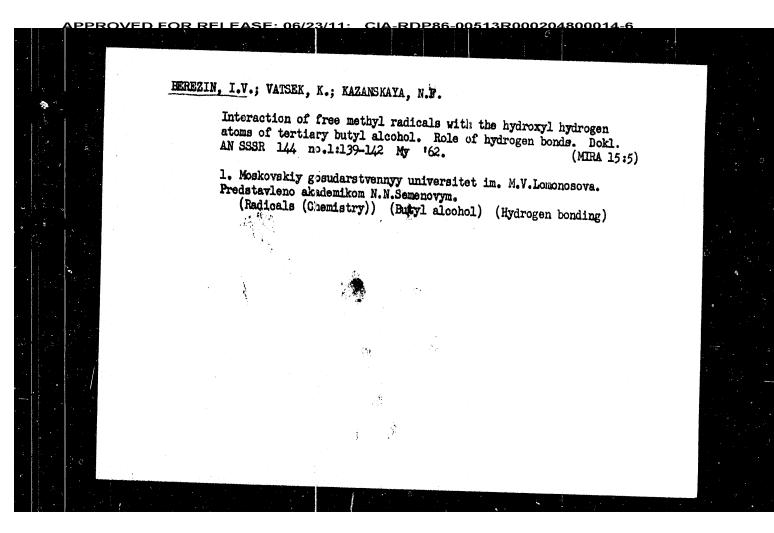
S/020/62/144/002/022/028 B101/B110

non-radioactive heptane gave more exact values than that of $^{\rm C}6^{\rm H}6$ with $^{\rm C}7^{\rm H}16^{\rm t}$ (2) The composition of the medium influences especially the ratio of the reaction constants of cis-decalin, methyl cyclopentane, benzene, and above all that of isooctane. (3) kH/kH depends on the structure of the hydrocarbon. The values referred to a secondary bond of heptane for 80°C are respectively: 0.1 and 3.7 for primary bonds of heptane and toluene; 1.0, 0.89, and 1.42 for non-conjugate secondary bonds of heptane, cyclohexane, and cyclopentane; 35.1, 38.5, and 95 for conjugate secondary bonds of cyclohexene, methyl cyclopentene, and 1,3-cyclohexadiene; 9.6, 13.7, 6.65, and 17.9 for tertiary bonds of methyl cyclohexane, methyl cyclopentane, trans-decalin, and cis-decalin; 0.067 and 0.068 for aromatic C-H bonds of benzene and toluene. (4) The low value of kH/kH for 2,2,4-trimethyl pentane (isooctane) (1.6 \pm 0.1 for $\begin{bmatrix} c_{7}H_{16} \end{bmatrix}$ = 100%, 4.2 for [RH] = 100%) indicates that the reactive bonds are screened by the methyl groups. There are 1 figure and 2 tables. The most important Englishlanguage references are: J. A. Meyer, V. Stannet, M. Szwarc, J. Am. Chem. Soc., 83, 25 (1961); E. W. R. Steacie, Atomic and Free Radical Reactions,

So

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S/020/62/144/002/022/028 B101/B110 5,3300 Berezin, I. V., and Dobish, O. AUTHORS: The influence of structure and medium on the reactivity of hydrocarkons with free methyl radicals in the liquid phase TITLE: Akademiya nauk SSSR. Doklady, v. 144, no. 2, 1962, 374-377 PERIODICAL: TEXT: The reactivity of hydrocarbons with CH3 (rate constant $k_{\sigma}^{\rm H})$ was determined to the reactivity of hydrocarbons with CH3 (rate constant $k_{\sigma}^{\rm H})$ mined by concurrent reactions using n-heptane-4t as standard. Free CH-3 radicals were obtained by thermal decomposition of acetyl peroxide at 60-90°C. The ratio of the rate constants is given by $k_0^H/k_{\rm hept}^H = 10.5 \left[(I_0 - I)/I \right] \cdot \left[(C_7 H_{16})/(RH) \right]$, where I_0 is the molar activity of CH_4 reacting with $C_7 H_{16} - t$ only, and I is that of CH_4 reacting with $C_7 H_{16} - t$ + RH. Results: (1) $k_{\sigma}^{H}/k_{hept}^{H}$ depends linearly on the composition of the mixture. Hence, only values extrapolated for zero concentration of the hydrocarbon in question can be intercompared. The reaction of C6H6-t with Card 1/3



EEREZIN, I.V.; DOBISH, D.

Reactivity of saturated hydrocarbons in their interaction with free methyl radicals in the liquid phase. Dokl. AN SSSR 142 no.1:105-108 Ja '62. (MIRA 14:12)

1. Moskovskiy gusudarstvennyy universitet im. M.V. Lomonosova. Predstavleno akademikom N.N. Semenovym. (Hydrocarbons) (Radicals (Chemistry))

EEREZIN, I.V.; KAZANSKAYA, N.F.

Kinetic isotopic effect of secondary tritium atoms of the n.heptane-t m:lecule in the liquid phase reaction with free methyl radicals, and the reactivity of 4-C - T bonds. Zhur. fiz.khim. 36 no.8:1800-1802 Ag '62. (MIRA 15:8)

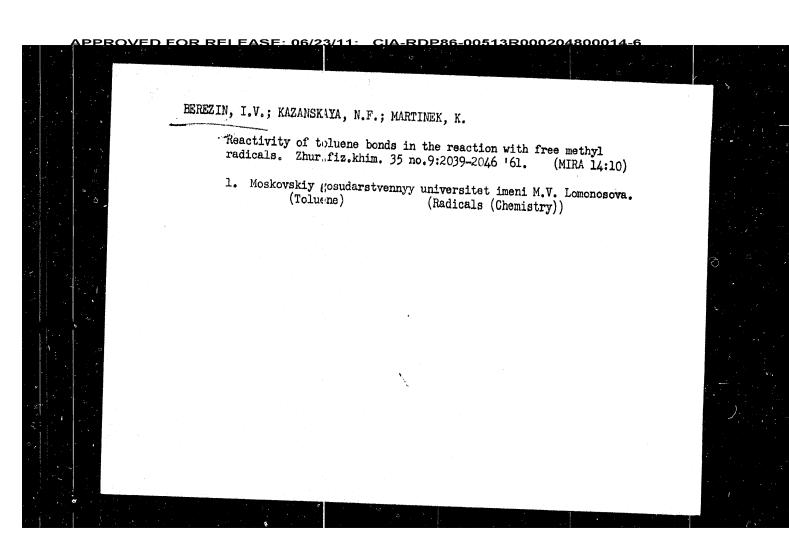
1. Moskovskiy gosudarstvennyy universitet imeni Lomonosova. (Tritium) (Heptane) (Redicals (Chemistry))

ANTONOVSKIY, V.L.; BEREZIN, I.V.; KAZANSKAYA, N.F.

Use of tritium for determining the relative constants of the rate of detachment of hydrogen atoms in organic compounds. Relative reactivity of parbon-hydrogen bonds of hydrocarbona in radical reactions. Izr.vys.ucheb.zav.; khim.i khim.tekh. 5 no.1:94-100 '62.

(MIRA 15:4)

1. Moskovskiy gosudarstvennyy universitet imeni Lomonosova, kafedra khimicheskoy kinetiki.
(Hydrogen bonding) (Hydrocarbons) (Radicals (Chemistry))



Investigation of the kinetics of ... S/081/62/000/004/004/087

substituted in toluene in the ortho, meta, and para positions and in the CH₃ group has been determined. The probable mechanism of the reaction between the CH₃ radical and the T atom in the hydroxyl group in trimethyl carbinol is considered and the abnormally high value of the factor of the The possibility of using T for approximate determination of the relative R of free radicals is demonstrated. [Abstracter's note: Complete translation.]

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 $[\cdot]_{i}$

Card 2/2

11.1510 11.0132

5/081/62/000/004/004/087 B149/B101

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AUTHORS:

Berezin I. V., Vatsek K., Kuo-Ch'u, Dobish O.,

Kazanskaya N. F.

TITLE:

Investigation of the kinetics of elementary free-radical

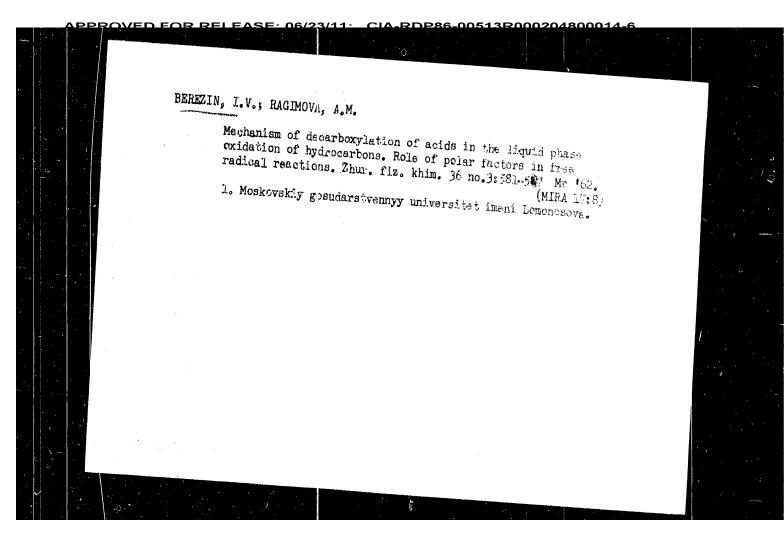
reactions in the liquid phase using tritium

PERIODICAL: Referativnyy zhurnal. Khimiya, no. 4, 1962, 62, abstract 4B429 (Tr. po khimii i khim. tekhnol. [Gor'kiy] no. I, 1961,

18-30)

The reactivity (R) of cis-decalin (I) and trans-decalin (II) in the reaction with free radical CH3, generated by decomposition of acetyl peroxide at 55-90°C was investigated with the help of tritium (T). The rate of reaction of I and II with CH3 was measured with reference to the standard reaction of breaking off a T atom from tritium-containing cyclohexane by the CH3 radical. The ratio of the rate constants for the reactions between CH3 and I and II is 1.56. The relative R of T atoms, Card 1/2

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PHASE I BOOK EXPLOITATION

SOV/6319

Berezin, Il'ya Vasil'yevich, Yevgen y Timofeyevich Denisov, and Nikolay Markovich Eminuel'

Okisleniye tsiklogeksana (Oxidation of Cyclohexane) Izd-vo Mosk. univ., 1962. 301 p. Errata slip inserted. 3500

Ed.: N. A. Korobtsova; Tech. Ed.: T. A. Kozlova.

PURPOSE: This book is intended for chemists and chemical engineers engaged in the industrial oxidation of cyclohexane.

COVERAGE: The book discusses current theory and technology of cyclohexane oxidation. Although the text is based primarily on non-Soviet materials, the discussion of kinetics is taken entirely from N. N. Semenov's theory of degenerate-branched chain reactions. The oxidation of cyclchexane is presented in the broadest range, e.g., from elementary reactions to the technological process. References are given at the end of each chapter.

Card 1/4

84691

Kinetic Isotopic Effects of Tritium in the Reaction of Hydrocarbons With Free Methyl Radicals in the Liquid Phase

S/020/60/134/004/017/023 B004/B064

and cyclopentane the authors conclude that the kinetic isotopic effect of tritium in the reaction with CH₃ for the unconjugated aliphatic secondary CH bonds is described by the relation i = 0.18 exp(3450/RT). In the case of cyclohexane a distinction is to be made between polar and equatorial bonds. Assuming that i equ = i sec = 0.18 exp(3450/RT) the following relation is found for i pol pol 0.48 exp(2300/RT). The largely deviating values for benzene and toluene are due to the effect of the aromatic cycle. There are 3 tables and 10 references:

ASSOCIATION:

Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

PRESENTED8

April 27, 1960 by N. N. Semenov, Academician

SUBMITTED:

March 28, 1960

Card 3/3

Kinetic Isotopic Effects of Tritium in the Reaction of Hydrocarbons With Free Methyl Radicals in the Liquid Phase

\$/020/60/134/004/017/023 B004/B064

hydrocarbons tagged with tritium was carried out at 55 \cdot 85°C. Table 1 gives data for $I_{C_6H_6}$, I_{CH_4} , and i at 85°C. Table 2 shows the values for benzene

and toluene at 55, 70, and 85° C. The function $\log(k^{H}/k^{T}) = f(1/T)$ was found to be linear. Table 3 compares the values obtained for different hydrocarbons at 85° C. The ratio A^{H}/A^{T} of the factors of the exponential function,

the difference $\Delta E = E^T - E^H$ of the activation energies, and i are given in Table 3:

Hydrocarbon	A^{H}/A^{T}	/E, kcal/mole	1
Benzene 1 toluene 1 cyclohexane 1 cyclopentane cycloheptane n-heptane (sec. bonds)	0.66	1570±100	6.0
	0.55	2200±100	12.1
	0.38	2700±100	17.2
	0.16	3500±350	22.8
	0.19	3430±250	23.5
	0.20	3400±130	23.2

From the data found for the secondary bonds of m-heptane, cycloheptane,

Card 2/3

84691 s/020/60/:34/004/017/023 B004/B064 11.1210 Antonovskiy, V. L. and Berezin, I. V. AUTHORS: Kinetic Isotopic Effects of Tritium in the Reaction of Hydrocarbons With Free Methyl Radicals in the Liquid Phase TITLE 3 Doklady Akademii nauk SSSR, 1960, Vol. 134, No. 4, pp. 860-863 PERIODICAL: TEXT: The authors determined the intramolecular kinetic effects $i = k^{H}/k^{T}$ in the reaction of liquid hydrocarbons with free methyl radicals. The reaction equations are written downs $RH + CH_3 \xrightarrow{k} R^\circ + CH_4$ (I) and RT + CH₃ $\stackrel{K}{\longrightarrow}$ R° + CH₃T (II). Assuming n reactive CH bonds in the RH molecule, and a concentration ratio of RT $\stackrel{K}{\nearrow}$ RH, the authors obtain for i the equation $i = I_{RH}/nI_{M}$ (1), where I_{RH} denotes the specific radioactivity the equation $i = I_{RH}/nI_{M}$ (1), where I_{RH} forming methane. Benzoyl perof RH, $I_{\underline{M}}$ the specific radioactivity of the forming methane. Benzoyl peroxide served as a source for the methyl radicals; its decomposition in Card 1/3

The Relative Reactivity of the C-H and C-T Bonds S/020/60/134/003/017/020 of n-Heptane, Benzene, Toluene, Ethylbenzene, and B004/B067 Liquid Phase

PRESENTED: April 27, 1960, by N. N. Semenov, Academician

SUBMITTED: March 28, 1960

The Relative Reactivity of the C-H and C-T Bonds 5/020/60/134/003/017/020 **83**903 of n-Heptane, Benzene, Toluene, Ethylbenzene, and B004/B067 Cyclohexane in the Interaction With CH3. in the

carried out to eliminate this specific effect of the aromatic cycle. ${\rm C_6H_5CH_3}$ and ${\rm C_6H_5CH_2CH_3}$ were tagged with tritium in their ${\rm CH_3}$ group, dissolved in small concentrations (0.134 - 4.00 wt%) in non-tagged ${^{\text{C}}}_{6}{^{\text{H}}}_{12}$, and reacted with CH;. Under these experimental conditions the relative rate constants for the tearing off of tritium did no longer depend on the composition (Tables 2,3). The following ratio was obtained for 85°C: $k_{\text{hept}}^{\text{T}}$: $k_{\text{eth.benz.}}^{\text{T}}$: $k_{\text{tol}}^{\text{T}}$ = 1: 14.5: 28. Thus, the phenyl group has a strongly activating effect on the hydrogen atoms of the ${\tt CH}_{z}$ group in toluene as well as in ethylbenzene. The high mobility of the primary hydrogen atoms in C6H5C2H5 night indicate a still unknown mechanism.

There are 2 figures, 3 tables, and 8 references: 5 Soviet and 3 US.

ASSOCIATION: Moskovskiy gouudarstvennyy universitet im.M.V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

Card 3/4

Liquid Phase

APPROVED FOR RELEASE: 06/23/11: CIA-RDP86-00513R000204800014-6

83903

The Relative Reactivity of the C-H and C-T Bonds S/020/60/134/003/017/020 of n-Heptane, Benzene, Toluene, Ethylbenzene, and B004/B067 Cyclohexane in the Interaction With CH_3° in the Liquid Phase

The equation $I_A/I_M = k_{6A}^H/k_{jA}^T + (k_{6B}^H/k_{jA}^T) \cdot ([B]/[A])$ (2) served for an experimental determination of the rate constant k, where I_A , I_M denote the activities of substance A and methane; $k_{6A}^H = \sum_{i=1}^{L} n_i k_i^H$; $k_{6B}^H = \sum_{i=1}^{L} n_1 k_1^H$. The authors determined (1) k_{6A}^H/k_{jA}^T , where CH_3^c was generated only in A; (2) k_{6B}^H/k_{6A}^H by generating CH_3^c in a mixture of A and B; (3) k_{6B}^H/k_{jA}^T , where a concentration ratio $[A] \ll [B]$ was chosen for a high activity of A. First, the authors carried out the reaction between non-tagged n-heptane, benzene, and toluene on the one hand, and tagged cyclohexane on the other. The values for the reaction of n-C7H₁₄ with $C_{6H_{12}}$ are given in Table 1. For saturated hydrocarbons $k_{hept}^H/k_{cyc.hex}^H$ is independent of the composition of the mixture. In the systems $C_{6H_6} - C_{6H_{12}}$ and $C_{6H_5} - C_{6H_{12}} - C_{6H_{12}}$ it was found that the quotients of k depended largely on the composition of the mixture (Figs. 1,2). Hence, a second experimental series was

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83903

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\$/020/60/134/003/017/020 B004/B067

AUTHORS:

Antonovskiy, V. L., Berezin, I. V., and Shevel'kova, L. V.

TITLE:

The Relative Reactivity of the C-H and C-T Bonds of

n-Heptane, Tenzene, Toluene, Ethylbenzene, and Cyclohexane in the Interaction With CH3 in the Liquid Phase

PERIODICAL:

Doklady Akademii nauk SSSR, 1960, Vol. 134, No. 3,

pp. 621-624

TEXT: The authors determined the rate constants k of the reactions of the $exttt{C-H}$ and $exttt{C-T}$ bonds on the following assumptions: In a system consisting of two organic compounds A and B, A has the number r of types of reactive C-H bonds, the bond of type j being tagged with tritium. Compound B is not tagged and has p types of C-H bonds. The total number of C-H bonds is assumed to be n. In this system, free methyl radicals are produced by thermal decomposition of benzoyl peroxide at 55° or 85°C. Equation (1) is written down for the composition [CH4]/[CH3T] of methane which was

formed according to the reaction equation $RH(\hat{T}) + CH_3 \longrightarrow R^* + CH_4(CH_3T)$.

Card 1/4

The Use of Tritium for Determining the Relative S/076/60/034/06/21/040 Rate Constants of the Clawage of Hydrogen BO15/B061 BO15/B061 of the Carbon - Hydrogen Bonds of n-Heptane

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

SUBMITTED: August 15, 1958

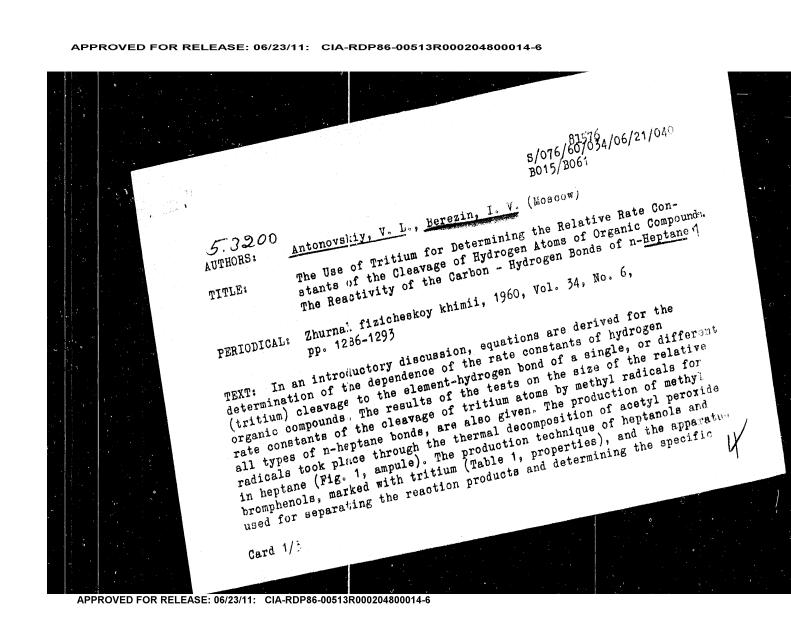
APPROVED FOR RELEASE: 06/23/11: , CIA-RDP86-00513R000204800014-6

81576

The Use of Tritium for Determining the Relative S/076/60/034/06/21/040 Rate Constants of the Bleavage of Hydrogen Atoms B015/B061 of Organic Compounds. The Reactivity of the Carbon - Hydrogen Bonds of n-Heptane

activity of methane and heptane (Fig. 2), are described. Measurements (Table 2) show that the by-reactions of the formation of methane can be neglected. The values of the rate constants of the reaction of the methyl radical with the C-T bond (calculated according to equation (10)) are given, as are the experimental values for the n-heptanes at 55° to 85°C (Table 3) in positions 1, 2, 3, and 4 substituted by tritium. O. B. Mesineva took part in some experiments. It was established that all secondary C-T bonds of n-heptane show practically the same reactivity in the temperature range 10-220°C (Table 4). The primary C-T bonds have, in the temperature range 55-85°C, a reactivity 10 to 12 times smaller than the secondary C-T bonds. $k^{\rm H}/k^{\rm T}=0.20~{\rm e}^{3400/{\rm RT}}$ was obtained for the hydrogen-tritium kinetic isotopic effect of the secondary bonds, which agrees with the corresponding value for cycloheptane (Ref. 26). A. N. Bashkirov, V. I. Vedeneyev, and V. V. Voyevodskiy are mentioned in the text. There are 4 figures, 4 tables, and 26 references: 8 Soviet, 15 American, 1 British, and 1 German.

Card 2/3



Reactivity of Toluene Bonds in the Interaction With Free Methyl Radicals
S/079/60/030/012/023/027

There are 1 table and 3 references: 2 Soviet and 1 US.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet (Moscow State

SUBMITTED: January 26, 1960

APPROVED FOR RELEASE: 06/23/11: CIA-RDP86-00513R000204800014-6

87537

Reactivity of Toluene Bonds in the Interaction With Free Methyl Radicals

S/079/60/030/012/023/027 B001/B064

constant for the separation of the hydrogen atoms from the toluene molecule (Ref.2). Since K_{σ}^{H} is independent of the character of tagging, it is possible to determine by this formula the ratio between the rate constants of the reactions of the nethyl radical with C - T bonds in different positions. The relative rate constants, the differences of the activity energies, and the ratio of the factors of the exponential function, the separation reactions of the tritium atoms and hydrogen on different bonds of the toluene molecule by free methyl radicals were determined. It was shown that the growth of the methane activity forming in the interaction of methyl and toluene, which is tagged with tritium in the cycle, is due to the addition of methyl to the π -bonds and the formation of products containing mobile tritium atoms. The following data are listed:

tagged with T	K_{i}^{T}/K_{n}^{T}	$\Delta E = E_{i}^{T} - E_{CH}^{H}$ $(cal/mole)^{3}$	AT/AHCH3
ortho- meta- para- CH3 group Card 2/3	0.76	4750±100	1±0.15
	0.22	7900±250	23±8
	1	4800±100	1.4±0.12
	156	2200±100	1.8

APPROVED FOR RELEASE: 06/23/11: CIA-RDP86-00513R000204800014-6

5.4300 1273 1160 1242

87537 S/079/60/030/012/023/027 B001/B064

AUTHORS:

Berezin, I. V., Kazanskaya, N. F., and Martinek, K.

TITLE:

Reactivity of Toluene Bonds in the Interaction With Free

Methyl Rad: cals

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 12, pp.4092-4093

TEXT: The authors investigated the reactivity of tritium atoms in different positions in the toluene molecule, in the reaction of the latter with free methyl radicals. The reaction proceeded by thermal decomposition of acetyl peroxide in a medium of toluenes tagged with tritium, at a temperature between 60-96°C (Ref.1). The methane formed was separated from the other reaction products and toluene, pumped into the counter, where its radioactivity was determined. The specific radioactivity of the toluene used in the experiments was determined in the same counter. The radioactivity of the toluene used for the experiments has the following ratio: $I_m/I_{tol} = K_1^T/K_0^H$, where K_1^T = the constant for the velocity with which the CH₃ radical separates tritium in the position i; K_0^H = the total Card 1/3

REFEZIN, I.V., RACINOVA, A.M.

Intermediate reactions of ketones in the liquid-phase oxidation of octadecane. Dokl.AN Aserb.SSR 16 no.1:19-22 '60. (MIRA 13:6)

1. Moskovskiy gosudarstvennyy universitet im. Lomonosova. Predstavleno akal. AN Azerbaydzhanskoy SSR M.F. Nagiyevym. (Ketones) (Octadecane) (Oxidation)

The problem of determining the solutions of the problem of determining the solutions of the problem of determining the solutions of the problem of determining the solutions are solved by the problem of determining the solutions of the problem of

Card 2/2

S/081/61/000/022/020/076 B102/B108

11.1510

AUTHORS:

Berezin, I. V., Kazanskaya, N. F.

TITLE:

The problem of determining the relative reactivity of free

radicals

PERIODICAL:

Referativnyy zhurnal. Khimiya, no. 22, 1961, 146, abstract

22Zh35 (Sb. nauchn, rabot. In-t Fiz.-organ, khimii AN BSSR,

no. 8, 1960, 88-92)

The determination of the reactivity of two radicals in the

 $R''H + X^\circ$ leads to the determinareactions $R^{6} + HX \xrightarrow{n} R^{6}E + X^{6}$ and $R^{6} + HX = 1$

tion of the ratio $\tilde{k_n}^\dagger/k_r$." Usually, the ratio of the reaction rate constants of the inverse processes is easily found. The problem is reduced to finding k_n^{-1}/k_n^{-1} from the known ratio k_0^{-1}/k_0^{-1} . Since the equilibrium constants of these processes are $k_{\ p}^{\ \ r}=k_{\ n}^{\ \ r}/k_{\ o}^{\ \ r}$ and

Card 1/2

The oxidation of cyclohexane

\$/595/60/000/000/004/014 £196/£535

included which gives yields of acid and ketone for the various methods of oxidation. A mathematical analysis of the reaction is made on the assumption that it is a simple chain reaction with a single intermediate and a single final product, the chain is assumed to be broken by recombination of the free radicals. Academicians B. A. Kazanskiy, G. S. Landeberg and N.N. Semenov are mentioned in the paper. There are 10 figures and 2 tables.

Test	Depth of oxidation	Yield of acid,%	Yield of ketone,%	<u>Table</u>
Autooxidation	14.8	30	no cone ; %	
Oxidation with St ₂ Co	NO 16	58 57	37	
Oxidation with I			23	
Oxidation with St ₂ Co + NO ₂	22	51.5	22	
- 2			27	

Card 5/5

The oxidation of cyclohexane

S/595/60/000/000/004/014 E196/E535

the catalyst (0.06 to 0.00023 mol %) showed that the higher the amount of catalyst, the faster the rate of reaction, demonstrating that, in the initial periods, it is a chain reaction whose rate of initiation is proportional to the concentration of dissolved catalyst. Similar results were obtained using cobalt adipate. The catalyst has thus two functions - initiation of the reaction and regulation of the proportions of the products. absorption of oxygen in the uncatalyzed reaction remains constant after the induction period; in the catalyzed reaction it rises to a maximum and decreases to a constant value which is less than that of the uncatalyzed reaction. This suggests a self-delaying action. To confirm this supposition the catalyst was removed from the reaction zone some time after initiation and the final constant velocity attained was found to be higher liquid phase oxidation, using NO2, was studied. A new method of stimulating saturated with NO₂ (0.4%) at a rate of 50 litres/hr. At 140°C the reaction was markedly accelerated. The method was also tried in combination with cobalt stearate catalyst. A table is

PROVED FOR RELEASE: 06/23/11: CIA-RDP86-00513R000204800014-6

The oxidation of cyclohexane

S/595/60/000/000/004/014 E196/E535

In glass vessels the hydroperoxide breaks down equally into cyclohexanol, formed entirely by the decomposition of cyclohexyl hydroperoxide, and cyclohexanone, from decomposition of the hydroperoxide and oxidation of cyclohexanol. Adipic acid is formed exclusively by oxidation of cyclohexanone whilst the esters are formed by direct esterification of the adipic acid with cyclohexanol. In a steel vessel, however, cyclohexanone is also formed by decomposition of the cyclohexyl hydroperoxide In the reaction with catalyzing salts, cobalt stearate dissolved in cyclohexane was used as catalyst. During the reaction, the cobal; changes into the trivalent state, and after a few minutes at 130°C the concentration of Co(III) becomes constant, then begins to decrease until after about 1.5 hours it is all once more in the divalent state. With the appearance of adipic acid the cobalt begins to precipitate as cobalt adipate, but part of the catalyst remains in solution throughout the reaction. The catalyzed and non-catalyzed oxidations differ as regards the reaction rate and concentrations of the inter-Experiments with different concentrations of mediate products.

Card 3/5

The oxidation of cyclohexane

S/595/60/000/000/004/014 E196/E535

saturated with water and adipic acid, which have limited solubilities in cyclohexane. As the reaction is a chain degradation-branching reaction, no single parameter can be used to characterize it. The maximum absorption rate of oxygen is a function of temperature and obeys the Arrhenius equation, with an activation energy of 27 kcal/mol. The log of the conversion coefficient to cyclohexyl hydroperoxide over the first part of the reaction varied linearly with the inverse of the temperature, with activation energy 29 kcal/mol. For the intermediate cyclohexanone, the log maximum concentration varied linearly with the inverse of the temperature, the activation energy being 8 kcal/mol. The transformation of the intermediate products was studied by the use of radioactive carbon as marker and the following sequence was found

Card 2/5

s/595/60/000/000/004/014 E196/E535

AUTHORS:

Emanuel', N.M., Berezin, I.V. and Denisov, Ye.T.

TITLE:

The oxidation of cyclohexane

SOURCE:

Vsesoyuznoye soveshchaniye po khimicheskoy pererabotke

neftyanykh uglevodorodov v poluprodukty dlya sinteza volokon i plasticheskikh mass. Baku, 1957. Baku, Izd-

vo AN Azerb.SSR, 1960, 143-156

The kinetics of oxidation of cyclohexane were investigated without using catalysts, with catalytic salts and with a stimulating gaseous initiation. The aim of this study was to gain more information on the oxidation of cyclohexane which is important in the production of cyclohexanone and adipic acid for the nylon fibre industry. A further aim was to determine the laws governing this simple liquid phase oxidation and to apply these laws to more complicated hydrocarbons. Without a catalyst satisfactory velocities can be attained at pressures of 10-100 atm and temperatures of 135-155°C. are cyclohexanone, cyclohexanol and cyclohexyl hydroperoxide. A second liquid phase appears when the reaction mixture becomes

Card 1/5

Determination of the Ratio of the Reaction Rate Con- SOV/20-127-1-33/65 stants When Tritium Atoms in n-Reptanes Are Torn off by the Methyl Radical

reactivity of all secondary C-H bonds of the n-paraffins. The mean constant isotope effect for the secondary CH-bonds of n-henters is illustrated by the relations

n-heptane is illustrated by the relation:

 $(k^{H}/k^{T})_{sec} = 0.20e^{-3400/RT}$

There are 2 figures, 1 table, and 6 references, 3 of which are Soviet.

ASSOCIATION: Moskovskiy (;osudarstvennyy universitet im. M. V. Lomonosova

(Moscow State University imeni M. V. Lomonosov)

PRESENTED: March 20, 1959, by N. N. Semenov, Academician

SUBMITTED: March 11, 1959

Card 3/3

Determination of the Ratho of the Reaction Rate Constants SOV/20-127-1-33/65 When Tritium Atoms in n-Heptanes Are Torn off by the Methyl Radical

heptane was measured by means of a counter. Table 1 shows the results obtained. The value of the reaction constant $\mathbf{k_2^T}$ with respect to the tritium detachment on the heptane 2-t was assumed as the unit. A part of the experiments made with heptane 2-t and 3-t was supervised by 0. B. Mesinova. Figures 1, 2 show

the linear dependence of the log $\frac{I_{CH_4}}{I_{C_7H_{16}}}$ on the absolute temperature with respect to heptane 1-t, 2-t, and 3-t. The

temperature with respect to heptane 1-t, 2-t, and 3-t. The constant values for k_1^T/k_2^T prove the equivalence of all secondary C-H- (C-T- resp) bonds of heptane in the temperature range of from 10 to 220°; this is directly indicative of the uniform

5(4) SOV/20-127-1-33/65 Antonovskiy, V. L., Berezin, I. V. AUTHORS: Determination of the Ratio of the Reaction Rate Constants When TITLE: Tritium Atoms in n-Heptanes Are Torn off by the Methyl Radical (Opredeleniye otnosheniy konstant skorostey otryva metil nym radikalom atomov tritiya n-geptanov) Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 1, pp 124-126 PERIODICAL: (USSR) As compared to the so very complicated reactions as are the ABSTRACT: oxidizing, chlorinating, sulfochlorinating processes (Refs 1-3) or as compared to the reaction rates in homogeneous series (Ref 4), the utilization of tritium offers the possibility of directly comparing the rate of hydrogen detachment by a free radical at a certain point of the compound. CH, radicals generated from acetyl peroxide were introduced into n-heptane, the jth CH-bond of which was marked with tritium. The methane thus formed was separated from the other gaseous (${\rm CO_2,C_2H_6}$) and liquid reaction products by traps cooled with liquid nitrogen. The specific activity of methane and of the marked

Degenerate Branching Mechanism on Liquid-phase Oxidation of Cyclohexane in a Steel Container

SOV/20-126-4-33/62

The velocity of the ramification is given by the velocity of equation 2, which practically proceeds from left to right. If, however, there are by-reactions, the velocity of ramification is smaller than the velocity of exidation of cyclohexanone. The velocity of oxidation of cyclohexanone is, according to the above considerations, of second order which is in good agreement with experimental data. The small value of the experimentally found activation energy (24 kcal per mol) agrees well with the character of the elementary reaction. There are 2 figures, 1 table, and 10 references, 8 of which are Soviet.

ASSOCIATION:

Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

PRESENTED:

January 29, 1959, by N. N. Semenov, Academician

SUBMITTED:

January 27, 1959

Card 4/4

SOV/20-126-4-33/62

Degenerate Branching Mechanism on Liquid-phase Oxidation of Cyclohexane in a Steel Container

> acylhydroperoxide, which decomposes at once, thus forming 2 new radicals:

5. R'CHO + R•
$$\rightarrow$$
 RH + R'C•O 6. R'C•O + O₂ \rightarrow R'C

000•

7. R'C
$$\stackrel{OO}{=}$$
 + HR \rightarrow R'C $\stackrel{OOH}{=}$ 8. R'C $\stackrel{OOH}{=}$ R'C $\stackrel{O^*}{=}$ + $\stackrel{OH}{=}$

9.
$$\mathbb{R}^{\bullet}\mathbb{C} \stackrel{0.}{=} 0$$
 + 2 $\mathbb{R}\mathbb{H} \longrightarrow \mathbb{R}^{\prime}\mathbb{C} \stackrel{OH}{=} 0$ + $\mathbb{H}_{2}\mathbb{O}$ + $\mathbb{H}_{2}\mathbb{O}$

The sequence of reactions 1-9 is so rapid that there are no measurable quantities of hydroperoxide of cyclohexanone, of the monoaldehyde of adipic acid and of peradipic acid in the system. As a result of all 9 equations it was found that instead of the used up radical ROO. three new radicals are forming which may react with oxygen:

Card 3/4

10. R. +
$$0_2 \longrightarrow R0_2$$

Degenerate Branching Mechanism on Liquid-phase Oxidation of Cyclohexane in a Steel Container

SOV/20-126-4-33/62

specific radioactivity of the latter determined. On the basis of the analysis results the authors suggest the following mechanism for the reaction investigated: The molecules of cyclohexanone are first attacked by free cyclohexylperoxide radicals. thus causing that a hydrogen atom in \(\infty \)-position to the keto group of cyclohexanone is separated:

1.
$$\bigcirc$$
=0 + R02° \longrightarrow R00H + \bigcirc =0 1'. \bigcirc =0 + HR \longrightarrow \bigcirc =0 + R.

The forming keto radical forms an lpha-keto hydroperoxide in

$$2 \cdot \stackrel{\bullet}{\longrightarrow} = 0 + 0_2 \longrightarrow \stackrel{00}{\longrightarrow} = 0 \qquad 3 \cdot \stackrel{00}{\longrightarrow} = 0 + HR \longrightarrow \bigcirc$$

Card 2/4

This monoaldehyde is easily oxidized under the formation of

AUTHORS: Berezin, I. V., Kazanskaya, N. F., Privalov, V. F. TITLE: Degenerate Branching Mechanism on Liquid-phase Oxidation of Cyclohexane in a Steel Container (O mekhanizme vyrozhdennykh razvetvleniy pri zhidkofaznom okislenii tsiklogeksana v stal'nom sosude) PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 126, Nr 4, pp 809-812 (USSR) ABSTRACT: The authors investigated the oxidation process of cyclohexanone during oxidation of cyclohexane in the liquid phase. The carefully purified cyclohexane was oxidized with air under a pressure of 10 atmospheres at 142°, 150° and 157° in a steel container. In the reaction mixture, cyclohexanone, cyclohexanol and hydroperoxide cyclohexyl were analyzed quantitatively (Ref 2). The kinetic curves of the products of oxidation at 150° and those of cyclohexanone are given in figure 1 at all three temperatures investigated. After a certain time cyclohexanone was added to oxidizing cyclohexane the former of which was marked by radioactive carbon in the carbonyl group. Subsequently samples of oxidized cyclohexane were taken and after precipi-

tation of cyclohexanone as 2,4-dinitro phenylhydrazone the

SOV/20-126-4-33/62

Card 1/4

5(4),5(3)

The Sequence of the Formation of Products in the Case of

the Liquid Acidification of Cyclohexane in Steel Vessels 507/20-126-3-38/69

ments were carried out in a steel vessel at 140°C and at a pressure of 10 at, and figure 1 shows the curve of the products in dependence on time. A further diagram (Fig 2) shows the variation with respect to time of molar activity, and table 1 shows the rate of the formation of alcohol at various points of time. Finally, the obtaining of cyclohexanyl is briefly discussed. There are 2 figures, 1 table, and 10 references,

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov) PRESENTED:

Janaury 29, 1959, by N. N. Semenov, Academician SUBMITTED:

January 27, 1959

sov/20-126-3-38/69 5(4) Berezin, M. V., Kazanskaya, N. F. AUTHORS: The Sequence of the Formation of Products in the Case of the Liquid Acidification of Cyclohexane in Steel Vessels (Posle-TITLE: dovatel'nost' obrazovaniya produktov pri zhidkofaznom okislenii tsiklogeksana v stal'nom sosude) Doklady Akademii nauk SSSR, 1959, Vol 126, Nr 3, PERIODICAL: pp 594 - 597 (USSR) It is said in the introduction that the essential part of the products of the acidification of hydrocarbons is formed by ABSTRACT: the decomposition of hydrogen peroxide. A scheme is given of a possible acidification of cyclohexane in the liquid state, after which a method is suggested for the synthesis of a radioactave hydrogen peroxide of cyclohexyl. This method is explained on the basis of the aforementioned scheme. The general radioactivity of the product is given in formula (1) as a function of molar radioactivity, and by formula (2) the timedependent variation of radioactivity is given. From these formulas, formula (5) is then developed for the rate at which the molar radioactivity of cyclohexane increases. The experi-Card 1/2

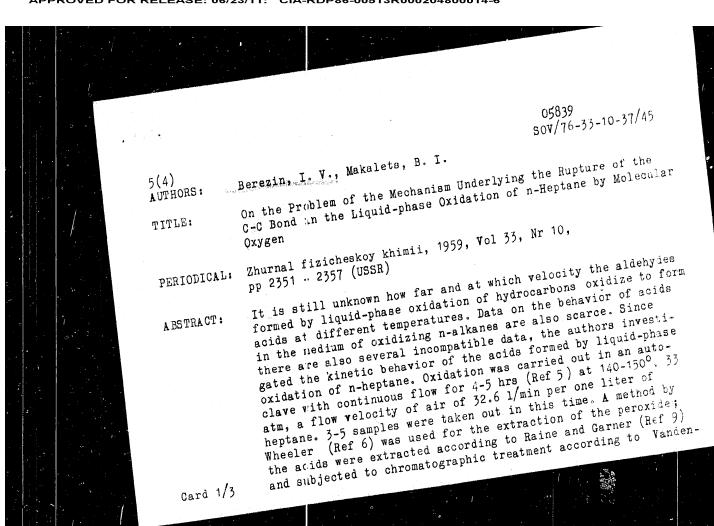
On the Problem of the Mechanism Underlying the Rupture SOV/76-55-10-37/45 of the C-O Bond in the Liquid-phase Oxidation of n-Heptane by Molecular Oxygen ASSOCIATION: Moskovskiy Rosudarstvennyy universitet im. M. Y. Lomonosova (Moscow State University imeni M. V. Lomonosov)

SUBMITTED: April 3, 1998

On the Problem of the Mechanism Underlying the Rupture SOV/76-33-10-37/45 of the C-C Bond in the Liquid-phase Oxidation of n-Heptane by Molecular Oxygen

heuvel (Ref. 10), using a silica gel prepared according to Ramsay (Ref. 11). The following acids were obtained: formic acid, acetic acid, propionic acid, butyric acid and valeric acid. Two layers were formed during the oxidation: an upper hydrocarbon layer and a lower layer of aqueous acid. Thus, analysis was complicated (Table: distribution of the oxidation products in the two layers). The authors plotted the kinetic curves of the accumulation of reaction products according to the reacting groups as well as of the accumulation of the various acids. Besides, experiments were made with the addition of butyric acid and butyric aldehyde (Figs 1-6). The ratio of acids remains fairly constant during the oxidation: $C_2 + C_1 : C_3 : C_4 : C_5 = 8:4:3:1$

The aldehydes were practically completely transformed into acids at a high velocity. It was found that the reaction mechanism underlying the rupture of the C-C bond during the liquid-phase oxidation of hydrocarbons, suggested in publications, may fully explain the ratio of the resultant acids. There are 7 figures, 1 table, and 12 references, 5 of which are Soviet.



SOV/80-32-4-33/47

The Oxidation of a Mixture of Cyclohexane and Cyclohexanol Into Adipic Acid

in the "anol head". The process of oxidizing "anol head" is to be carried out with continuous removal of adipic acid obtained in order to prevent its burning into lower dicarboxylic acids, and the process thereby acquires a continuous character.

There are 3 sets of graphs and 7 Soviet references.

SUBMITTED:

November 1, 1957

5(3)

SOV/80-32-4-33/47

AUTHORS:

Berezin, I.V., Denisov, Ye.T., Suvorova, S.N., Smolyan, Z.S. and Emanuel', N.M.

TITLE:

The Oxidation of a Mixture of Cyclohexane and Cyclohexanol to Adipic Acid (Dkisleniye smesi tsiklogeksana i tsiklogeksanola v

PERIODICAL:

Zhurnal prikladnoy khimii, 1959, Vol 32, Nr 4, pp 888-892 (USSR)

ABSTRACT:

Production of monomers for plastics and synthetic fibers is one modern chemistry. The utilization of various waste materials can contribute to the solution of this task. One of these waste materials is the mixture of cyclohexane, 80 mol.%, and cyclohexanol, 20 mol.%. The authors studied the kinetics of the oxidation of this mixture, called "anol head", with an aim of obtaining cyclohexane and adipic acid. The oxidation was carried cut in an autoclave at a pressure of 20 atm by molecular oxygen at temperatures of 130 and 150°C. Kinetic curves of accumulation of the reaction products were obtained and the possibility of producing adipic acid by oxidizing the "anol head" was proven. It was shown that some peculiarities in the oxidation kinetics were determined wholly by the concentration of cyclohexanol

BEREZIM, I.V.; RAGIMOVA, A.M.

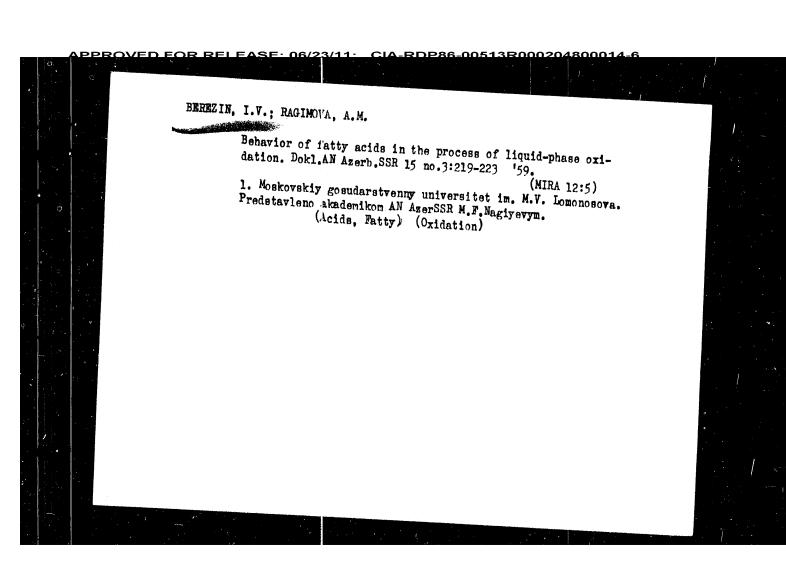
Studying the reactions of certain intermediate products in the process of liquid phase exidation of octadecane. Dokl.AM

Azerb.SSR 15 no.11:1015-1017 '59. (MIRA 1):4)

1. Moskovskiy gosudaratvennyu universitet. Predstavleno akademikon AN Azerbaydzhanskoy SSR M.F.Magiyavym.

(Esterification) (Decanoic acid)

BEREZIN, I.V.; RAGIMOVA, A.M. Formation of esters during liquid-phase oxidation of octadecane. Dokl. AN Azerb. SSR 15 no.9:815-819 '59. (MIRA 13:2) 1. Kafedra khimicheskoy kinetiki Moskovskogo gossudarstvennogo universiteta imeni Lomonosova, Predstavleno akademikom AN Azerbaydzhanskoy SSR M.F. (Octadecane)



The Price Littlian Conterence of the Price Littlian Conterence of the Price Littlian Conterence of the Ventuck Education (Ventuck Education) (Vent	Card 1/4 Indication of Raidousies incloses by Timination as \$-Diversions. ***Indication of Raidousies incloses by Timination as \$-Diversions. ***Indication of Raidousies included in the result of Raidousies of College Timination of Raidousies. ***Indication of Raidousies of College Timination of Raidousies. ***Indication of Raidousies of Timination of the Raidousies included in the Raidousies of Timination of Raidousies of Timination of Raidousies in the Raidousies of Timination of Raidousies of Timination of Raidousies of Timination of Raidousies of Timination of T	11 K. 2. 2. 2. 2. 2. 2. 2. 2. 2. 2. 2. 2. 2.	CHARL Of Chestand Institution of Transporter Transporter Transporter Transporter Transporter Transporter Constants of the Sparsion of Ocean-Indiana Constants of the Sparsion of Ocean-Indiana Constants of of Ocean-Ind

Paraffin Oxidution Initiated by Chlorine During the Initial Stage

curves of acid forsation is due to the presence in "Keppen".

There are 8 graphs, 1 diagram and 4 Soviet references.

SUBMITTED: December 20, 1956

Card 2/2

AUTHORS:

SOV/80-59-1-28/44 Berezin, I.V., Vagner, G. and Emanuel', N.M.

TITLE:

Paraffin Oxidation Initiated by Chlorine During the Initial

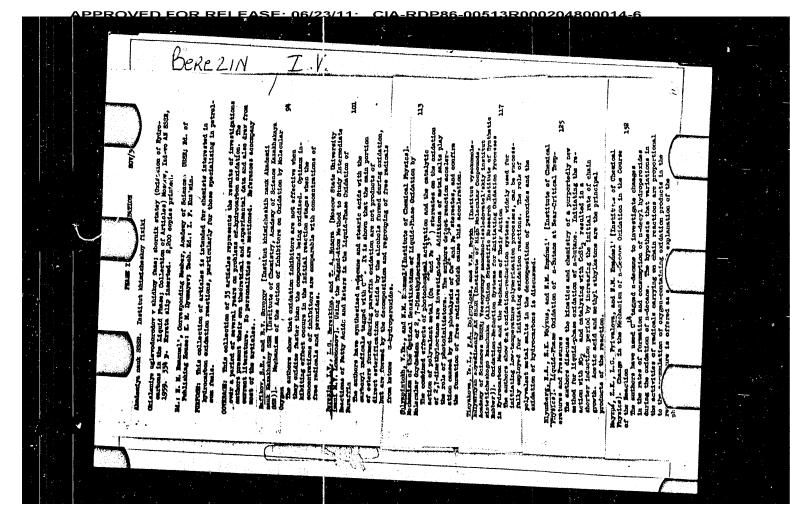
States of the Reaction (Okisleniye parafina, laitalirevanceye khlorom v nachal'nyy period razvitiya realtani)

PERIODICAL:

Zhurnal prikladnoy khimii, 1959, Mr 1, pp 173-180 (USSR)

ABSTRACT:

The method of stimulating liquid-phase oxidation reactions by means of small admixtures to the air of certain catalyzing gases (NO2, HBr, etc) was named the method of gas initiation Ref. 17. The present investigation was aimed at establishing main regularities of the initiation effect caused by acmixtures of chlorine in the oxidation process of lignite paralle fin of the "Kepsen" type (East Germany). As the main products of oxidation are aliphatic acids, the principal attention wan paid to the kinemics of their formation and accumulation. The results of experiments are presented in graphical form. It can be concluded that the gas initiation of the reaction by chlorine has a strong stimulating effect on the paraffin oxidation process; at that the initiation is brought about during a short initial period in the development of the process. The accumulation of acids is described by the kinetic curves obtained experimentally. It was established that the low maximum effect in the kinetic



A Method of the Quantitative analysis of Cyclohexanone and Cyclohexanol in Oxidation Products of Cyclohexane by Means of Infrared Absorption Spectra (Moscow State University imeni & V. Lomonosova (Moscow State University imeni & V. Lomonosova September 14, 1956)

1. Cyclohexanones—Quantitative analysis 2. Cyclohexanols—Quantitative analysis 3. Cyclohexanes—Reduction 4. Infrared spectrum:

A Method of the Quantitative Analysis of Cyclohexanone and Cyclohexanol in Oxidation Products of Cyclohexane by Means of Infrared Absorption Spectra

tion of the concentration of the substances was conducted according to the law by Lambert-Beer, employing the extinction coefficient. At higher concentrations of alcohol the sample had to be diluted. A comparison of the results obtained with that of other methods showed that the determination is not disturbed by the presence of peroxides. On the other hand, a ketone is present in the sample, the cyclohexanone. The presence of other oxidation products does not disturb its determination. A hydration is proposed in order to prevent an increase of the results caused by the influence of substantial amounts of esters and acids. In order to be able to determine the ester content, the extinction coefficient of the carbonyl band was approximately determined, as well as of the mono- and dicyclohexyl esters of adipic acid. The analysis as to contents of ketones and esters in the oxidation mixture can only be conducted at optical densities below 0,3, where the spectral bands separate from each other, in case they are present simultaneously. There are 5 figures, 4 tables, and 8 references, 4 of which are Soviet.

AUTHORS:

PPROVED FOR RELEASE: 06/23/11:

Berezin, I. V., Kazanskaya, N. F., Meluzova, G. B.

CIA-RDP86-00513R000204800014

TITLE:

A Method of the Quantitative Analysis of Cyclohexanone and Cyclohexano. in Oxidation Products of Cyclohexane by Means of Infrared Absorption Spectra (Metod kolichestvennogo analiza tsil:logeksanona i tsiklogeksanola v produktakh okisleniya tsiklogeksana po spektram pogloshcheniya v infrakrasnoy oblasti)

PERIODICAL:

Zhurnal fizicheskoy khimii, 1958, Vol. 32, Nr 6, pp.1218-1225

ABSTRACT:

A method of analysis serving in a number of kinetic investigations was leveloped. An infrared spectrometer of the type IKS-1 with automatic recording equipment EPP-09 and with cuvettes of special construction was used. A description of the apparatus and a schematic figure are given. By making use of the different intensity of the spectral bands the analysis could be conducted in such a way as to determine ketone and alcohol in the same cuvette, which is important because of the small amount of sample substance. The determina-

Mechanism of the Oxidation of the Acids With Molecular Oxygen SOV/79-28-10-19/60 at the β -carbon atom. In the decarboxylation of the acid a methyl ketone is formed that has one carbon atom less than the acid. The oxidizability of the acid depends on its structure. The acetic acid is practically inert. The yield of the n-valeric acid activated with radioactivated carbon in the on -position amounted to 23 %. There are 1 table and 9 references, 3 of which are Soviet. ASSOCIATION: Moskovsk: y gosudarstvennyv universitet (Moscow State University) SUBMITTED: August 8, 1957 Card 3/3

Mechanism of the Oxidation of the Acids With Molecular Oxygen

SOV/79-28-10-19/60

of the scid molecules. As the acids are not only used up in the reaction process but also are formed as such as a consequence of the oxidation of hydrocarbon, the favorable solution of this problem consists of employing the method of isotopic indicators. A simple method was chosen that made the analytical part of the work considerably easier, i. e. the oxidation of n-butyric and n-valeric acid in n-heptane medium. To observe the behaviour of the functional group as well as that of the hydrocarbon chain of the acid an n-butyric acid with radioactivated carbon in the carboxyl, and an n-valeric acid radioactivated in the &-position were synthesized. Moreover, an acetic acid was produced that was radioactivated in the carboxyl in order to prove its oxidizability under the conditions given. Concluding, the following results are mentioned: The acids are subjected to a quantitative decarboxylation in the medium of the oxidizing hydrocarbon. In the activation of the carboxyl with radioactivated carbon CO2 is the only active gaseous reaction product. According to this separated gas the behaviour of the acid carboxyl in any complex system of the oxidation products of hydrocarbons can be classified. The oxidizing reagent attacks the acid molecule

AUTHORS:

Berezin, I. V., Makalets, B. I.,

SOV/79-28-10-19/60

Chuchukina, L. G.

TITLE:

Mechanism of the Oxidation of the Acids With Molecular Oxygen in the Medium of n-Heptane (Mekhanizm okisleniya kislot

molekulyarnym kislorodom v srede n-geptana)

PERIODICAL:

Zhurnal obshchey khimii, 1958, Vol 28, Nr 10, pp 2718-2723

(USSR)

ABSTRACT:

From the papers known on the oxidation of acids with bound and air oxygen in the presence of catalysts (Refs 1-4) it may be seen that the oxidation mechanism of the acids depends on the conditions of the experiments. Therefore the rules governing the oxidation of the single acids in the presence of catalysts with different oxidizing agents may not be extended without earlier examination to the case where the oxidation of the acids takes place in the medium of an oxidizing hydrocarbon. It was of interest to the authors to investigate the chemical nature of the oxidation of acids in this respect, to compare it with data in publications and thus to discover the fundaments of the oxidation mechanism in dependence on the character of the reaction and the structure

The Determination of the Ketones, Esters, and Acids in the Products of the Oxidation of Paraffin Hydrocarbons in the Liquid Phase by Means of the Measuring of the Absorption Spectra in the Infrared Range

ASSOCIATION:

Moskovski; gosudarstvennyy universitet im. M. V. Lomonosova

(Moscow State University imeni M. V. Lomonosov)

SUBMITTED:

May 16, 1957

1. Ketones -- Determination 2. Esters -- Determination

3. Acids--Determination 4. Organic compounds--Spectra

5. Infrared spectroscopy

Card 4/4

sov/75-13-4-19/29

The Determination of the Ketones, Esters, and Acids in the Products of the Oxidation of Paraffin Hydrocarbons in the Liquid Phase by Means of the Measuring of the Absorption Spectra in the Infrared Range

 $^+$ 3 cm $^{-1}$, and that of carboxylic acids is at a frequency of 1713 + 2 cm⁻¹. The extinction coefficients and the contours of the bands were measured for individual substances and for mixtures of compounds with a carbonyl group (by means of an apparatus of the type IKE -11, and automatic recorders of the type RPP-09 (Ref 3)). The influence exerted by the mixing of the frequencies of the components on the extinction coefficient of the absorption bands of the mixture was explained. Also the correction values and the extinction coefficients in mixtures of ketones, esters, and acids were found. Furthermore methods for the removal of the acids are described by which fact the accuracy of the determination of ketones and esters is increased. The whole complex of problems is dealt with in detail. N. K. Man'kovskaya supplied samples of oxidized paraffin and cf acids for the experiments. This is acknowledged by the authors. There are 2 figures, 6 tables, and 13 references, 7 of which are Soviet.

Card 3/4

APPROVED FOR RELEASE: 06/2<mark>3/11: CIA-RDP86-00513R000204800014-6</mark>

The Determination of the Ketones, Esters, and Acids in the Products of the Oxidation of Paraffin Hydrocarbons in the Liquid Phase by Means of the Measuring of the Absorption Spectra in the Infrared Range

which conditions must be met in the kinetic investigations as well as in the practical work of the oxidation of high molecular paraffin hydrocarbons. Substances of different origin were used for taking the spectra: acetone, methyl-ethyl ketone, dibutyl ketone, ethyl acetate, amyl acetate, butyric acid, stearic acid, stearone (synthesized according to Ref 5), methyl stearate; further a mixture of synthetic fatty acids of different composition which mainly consisted of not ramified carboxylic acids, and which had been obtained by the oxidation of a mixture of high molecular paraffins (at the SZHK Kombinat at Shebekino), methyl esters of the synthesized acids, esters of the synthesized fatty acids with the alcohol C₁₃, as well as a

mixture of ketones with a mean molecular weight of 249. It was found that ketones and esters may be quantitatively determined in mixtures of oxidation products in paraffins on the basis of the absorption spectrum of the >C=O bond. The absorption band of the keto group of aliphatic ketones is at a frequency of 1718 - 3 cm -1, that of esters has one of 1738 +

AUTHORS:

Berezin, I. V., Meluzova, G. B.

SOV/75-13-4-19/29

TITLE:

The Determination of the Ketones, Esters, and Acids in the Products of the Oxidation of Paraffin Hydrocarbons in the Liquid Phase by Means of the Measuring of the Absorption Spectra in the Infrared Range (Opredeleniye ketonov, efirov i kislot v produktakh zhidkofaznogo okisleniya parafinovykh uglevodorodov po spektram pogloshcheniya v infrakrasnoy oblasti)

PERIODICAL:

Zhurnal anuliticheskoy khimii, 1958, Vol. 13, Nr 4, pp. 476-484 (USSR)

ABSTRACT:

The methods of the functional analysis of mixtures of oxygen-containing organic compounds on the basis of the absorption spectrum in the infrared range (Refs 1, 2) as described in publications have a number of disadvantages: they either have an insufficient accuracy or they may be used only in the absence of carboxylic acids. The latter makes impossible the employment of these methods in the analysis of oxidation products of saturated hydrocarbons, the acid content of which, as a rule is high. In the present paper the authors elaborate a method for the quantitative determination of ketones, esters, and acids which secures sufficient accuracy and a quick analysis,

On the Determination of the Reactivity of Hydrogen Atoms in Organic Compounds.

The Kinetic Isotope Effect of Tritium in Radical Reactions of the Cyclo
at the Moscow State University imeni M. V. Lemonosov)

SUBMITTED: April 12, 1958

CIA-RDP86-00513R000204800014

AUTHORS:

Antonovskiy, V. L., Berezin, I. V.

sov/156-58-4-30/49

TITLE:

On the Determination of the Reactivity of Hydrogen Atoms in Organic Compounds. The Kinetic Isotope Effect of Tritium in Radical Reactions of the Cycloparaffins (Ob opredelenii reaktsionnoy sposobnosti atomov vodoroda organicheskikh soyedineniy. Kineticheskiye izotopnyye effekty tritiya v radikal nykh reaktsiyakh tsikloparafinov)

PERIODICAL:

Nauchnyye doklady vysshey shkoly. Khimiya i khimicheskaya tekhnologiya, 1958, Nr 4, pp 731-735 (USSR)

ABSTRACT:

A method for the quantitative determination of the relative reactivity of hydrogen atoms in organic compounds was suggested. The relative reactivity of hydrogen atoms in cyclopentane and cyclohexane was determined. The kinetic hydrogen tritium isotope effect in the reactions CH_{3} with cyclopentane, cyclo-

hexane and cycloheptane was measured. There are 2 tables and

6 references, 2 of which are Soviet.

ASSOCIATION:

Card 1/2

Kafedra khimicheskoy kinetiki Moskovskogo gosudarstvennogo universiteta im. M. V. Lomonosova (Chair of Chemical Kinetics SOV/156-58-2-29/48
Almotic leaters affect of Mydrogen. The Reaction of Benzene-t With the Redcal of Wethyl

CIA-RDP86-00513R000204800014-6

SOV/156-58-2-29/48

Kinetic Isotopic Effect of Hydrogen. The Reaction of Benzene-t With the Radical of Mathyl

> active radicals as OH,. .OH and others which form a solid bond with the hydrogen atom (Ref 2). The presence of substituents exercises a considerable influence on the mechanism of stripping. This may lead to the formation of an intermediary adduct and can direct the reaction to the way of scheme b) (Ref 4). Methyl radicals are formed in a carbonic acid solution in connection with the decomposition of the used acetyl peroxide. Part of them strips the hydrogen atoms and forms methane; the remaining ones recombine with other radicals or affiliate with unsaturated molecules amongst which is the benzene-ring. Concludingly, the method of carrying out the experiment is described. There are 1 figure, 1 table, and 10 references.

ASSOCIATION: Kafedra khimicheskoy kinetiki Moskovskogo gosudarstvennogo universiteta im. M. V. Lomonosova (Chair of Chemical Kinetics of Moseow State University imeni M. V. Lomonosov)

SUBMITTED: Card 3/4

October 29, 1957

Kinetic Isotopic Effect of Hydrogen. The Reaction of Benzene-t With the Radical of Methyl

takes place in a single stage by bursting of the C-H-compound which must lead to a great isotopic effect. In the present report, the isotopic effect was measured - as given in the title - according to the reaction CH_3 + C_6H_6 -t CH_4 - + C_6H_5 -, (1) at 85,00 ± 0,05°. The calculation was carried out according to the formula $\frac{k_1}{k_1}$ specific activity of benzene-t (specific activity of CH_4 -t) x 6 where 6 - in-

dicates the number of hydrogen atoms in the $C_{6}H_{6}$ -molecule. The test-results are given in table 1. Two test-series were made with initial concentrations of acetyl-peroxide: 0.025 and 0.01 mol/l. As can be seen from table 1, the amount of the specific activity of the separated methane (and consequently also the amount of the isotopic effect) practically does not depend on the intensity of decomposition of acetyl-peroxide. The average value of the isotopic effect amounts to 6.02 \pm 0.07. It hence follows that the stripping of the hydrogen atom from benzene takes place by a direct bursting of the C-H-compound according to scheme a). Such a mechanism of stripping is characteristic for such highly

Sard 2/4

AUTHORS: Antonovskiy, V. L., Berezin, I. V. 507/156-58-2-29/48 TITLE: Kinetic Isotopic Effect of Hydrogen (Kineticheskiy izotopnyy effekt vodoroda) The Reaction of Benzene-t With the Radical of Methyl (Reaktsiya benzola-t s metil'nym radikalom) PERIODICAL: Nauchnyye doklady vysshey shkoly. Khimiya i khimicheskaya tekhnologiya, 1958, Nr 2, pp. 320-323 (USSR) ABSTRACT: The study of these effects forms the indispensable first stage in connection with the use of hydrogen-isotopes for the investigation of the reactivity of different C-H-compounds. Due to the knowledge of these effects the mechanism of the chemical reaction can also be clarified more thoroughly. The separation of the hydrogen atom from the aromatic nucleus by a radical at present is explained by means of 2 schemes (Refs 1-4): a) a direct stripping of the hydrogen according to which the phenyl-radical enters reactions which end by a radical recombination; b) first of all the radical R affiliates to the aromatic nucleus and forms the adduct I which subsequently reacts with the other radical and forms $R\!-\!C_6H_5$ and $R^{\dagger}H$. The stripping of hydrogen according to the reaction b) needs not take place under a sub-

stantially isotopic effect. According to scheme a) the reaction

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Investigations in the Field of the Stereochemistry of Cyclic Compounds.

62-2-9/28

were drawn,

There are 4 tables and 10 references, 6 of which are Slavic.

ASSOCIATION:

State University imeni M.V. Lomonosov, Moscow (Moskovskiy gosudarstvennyy universitet imeni M.V. Lomonosova) and Institute for Organic Chemistry AN USSR imeni H.D. Zelinskogo (Institut organicheskoy khimii imeni N.D. Zelinskogo Akademii

nauk SSSR).

SUBMITTED:

September 7, 1956

AVAILABLE:

Library of Congress

1. Stereochemistry-Cyclic compounds 2. Lactones-Structural analysis 3. Cyclic compounds-Structural analysis

Card 2/2

APPROVED FOR RELEASE: 06/23/11: CIA-RDP86-00513R000204800014

Benezin, I.V.

AUTHORS:

Kucherov, V. F., Berezin, I. V., Nazarov, I. N.

62-2-9/28

TITLE:

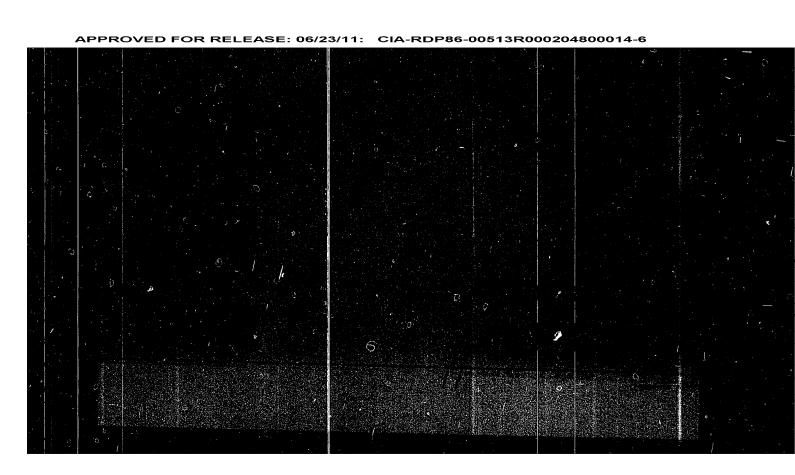
Investigations in the Field of the Stereochemistry of Cyclic Compounds (Issledovaniye w oblasti stereokhimii tsiklicheskikh soyedineniy). Report 19: Infrared Spectra of Cyclic Lactones (Soobshcheniye 19. Infrakrasnyye spektry tsiklicheskikh laktonov).

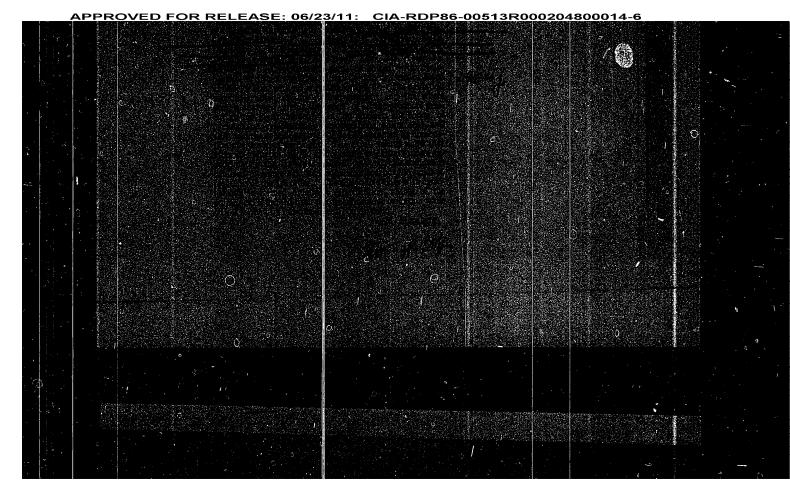
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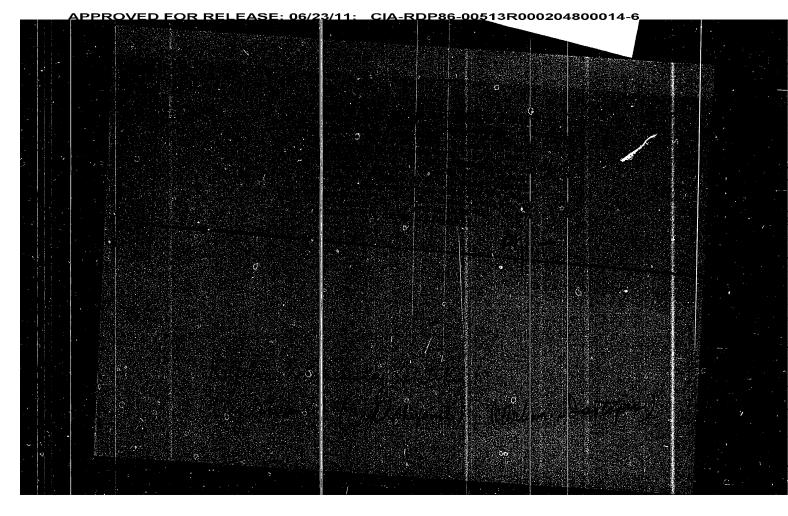
Izvestiya AN SSSR Otdeleniye Khimicheskikh Nauk, 1958, Nr 2, pp. 186-191 (USSR).

ABSTRACT:

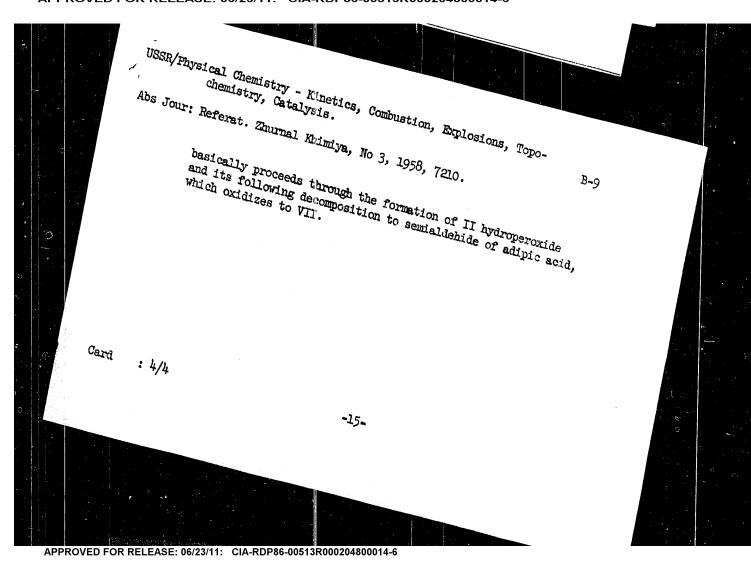
As was already shown in a paper published earlier the method of infrared spectroscopy can successfully be employed for proving the structure of lactones. For the purpose of the systematic investigation of the dependence of the infrared spectra on the structure of diverse polycyclic lactones the authors examined the spectra of the carboxyl-frequencies. They determined some structural regularities of the carboxyl-frequencies of this type of compounds. On the basis of the analysis of the infrared spectra of lactones-1 and 2-methyldecaline-1, 2-dicarboxylic acids their configuration was determined and from it the conclusions on the stereochemistry of the diene condensation of 1-vinyl-A-cyclohexane with citracon anhydride







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USSR/Fitting Out of Laboratories - Instruments.
Their Theory, Construction, and Use.

H-

Abs Jour : Ref Zhur - Khimiya, No 3, 1957, 8649

can be varied by the insertion of gaskets. An apparatus has been constructed for measuring the thickness and taper of the cell, using the micrometer attachment of the microscope. The authors are of the opinion that the thickness of the cell can be measured with an accuracy of \pm 1 \wedge .

Card 2/2

· BEREZIN, I. Y.

USSR/Fitting Out of Laboratories - Instruments.

Their Theory, Construction, and Use.

Abs Jour : Ref Zhur - Khimiya, No 3, 1957, 8649

Author : Berezin, I.V., and Meluzova, G.B.

Title : A Cell for Quantitative Spectroscopic Analysis in the Infrared Region and Description of Apparatus for Measuring

H-

the Thickness and Taper of the Cell.

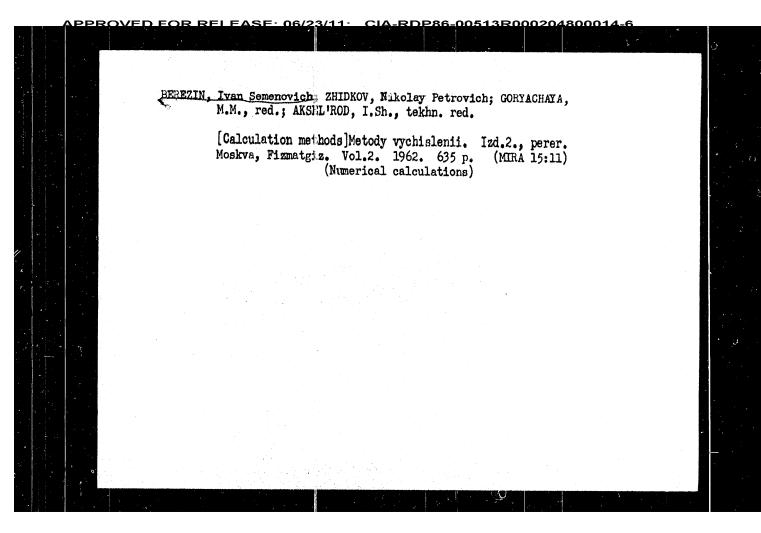
Orig Pub : Zh. analit. khimii, 1955, Vol 10, No 4, 262-264.

Abstract: An infrared cell is described consisting of two crystal windows cemented to metal plates with Ag or Cu amalgam; the plates are attached to both sides of a cylinder with screws. Two holes fitted with ground stoppers are drilled into the cylinder and are used for filling and washing the cell. The thickness of the cell is equal to the

distance between the windows and is determined by the thickness of the cylinder; the thickness of the cell

Seres WILV USSR/Chemistry - Physical chemistry **Card** 1/1 Pub. 22 - 20/45 Authors Peresin, I. V. Title ! Certain data on the kinetics of acylation of alcohols with 3,5-dimitropenyoya oliterelde Periodical : Dok. AN SSSR 99/4, 563-564, Dec 1, 1954 Abstract Data on the kinet os of scylation of certain alcohols, with various acylating media, are presen ed. Paranitro- and 3,5-dimitrobenzovi chloride plus small amounts of pyridi e were found to be the most active acylating media. The possibility of using 3,5-dimitrobenzoyl chloride for quantitative determination of primary and secondary alcohols and mono-atomic phenols is briefly discussed. One U. SR reference (1953). Table, graph. Institution: The M. V. Lomonosev State University, Moscow Presented by: Academician N. N. Semenov, July 20, 1954

ISUR/oncessor: Phys. cal-Olient Card 1/1 Authors : Beresin, L. V., and Denisov, B. T. 1 Basic products of liquid-phase exidation of cyclohexane with atmospheric oxygen and the role of these products in processes of phase-formation 1 Dokl. AN SSSR, 97, Rd. 2, 273 - 275, July 1954 Periodical : Two layers (upper and lower) are formed during the oxidation of cyclohexene with atmospheric oxygen; the upper layer represents a solution of reaction Abstract products in cyclinexame; the lower layer consists of liquid exidation products and a cone derable amount of solid acids. Quantitative separation of upper layer products showed that 95 mol. % of all alcohols consisted of cyclohexanol and 97 mol. % of all carbonyl compounds consisted of cyclohexane. The lower layer contained the same products plus adipic and formic acids. Five references. Tables. Institution : The M. V. Lomonos by State University, Moscow Presented by : Academician N. N. Semenov, March 20, 1954



PPROVED FOR RELEASE: 06/23/11: CIA-RDP86-00513R000204800014-6

PHASE I BOOK EXPLOIDATION SOV/3859

Berezin, Ivan Semenovica, and Nikolay Petrovich Zhidkov

Metody vychisleniy, t. 2 (Computation Methods, v. 2) Moscow, Fizmatgiz, 1959. 620 p. 10,000 copies printed.

Eds.: B. M. Budek and A. D. Gorbunov; Tech. Ed.: N. Ya. Murashova.

PURPOSE: This book is intended as a textbook for students in divisions of mechanics and mathematics and of physics and mathematics who are specializing in computational mathematics, and also for those interested in the theory and practice of numerical methods.

COVERAGE: The book is the second of two volumes. The authors analyze numerical methods of solving systems of linear algebraic equations, equations of higher degrees, and transcendental equations. They also discuss numerical methods for finding eigenvalues, approximate methods of solving ordinary differential equations, partial differential equations, and integral equations. No personalities are mentioned. References are given after each chapter.

· Calculation Methods, Vol. 1 (Cont.) SOV/3982 Assistant N. S. Bakhalov. The authors also thank Professor A. N. Tikhonov, Corresponding Member of the Academy of Sciences USSR, and Docent B.M. Budak. References accompany each chapter. TABLE OF CONTENTS: Preface 7 Introduction 9 1. The subject of computational mathematics 9 2. Method of computational mathematics 10 1. Functional metric spaces 10 2. Functions defined in functional spaces 12 3. Method of computational mathematics 13 3. Computational means 16 1. Arithmometer. Key-type computers 17 Card 2/17

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PHASE I BOOK EXPLOITATION

SOV/3982

Berezin, Ivan Semovich, and Nikolay Petrovich Zhidkov

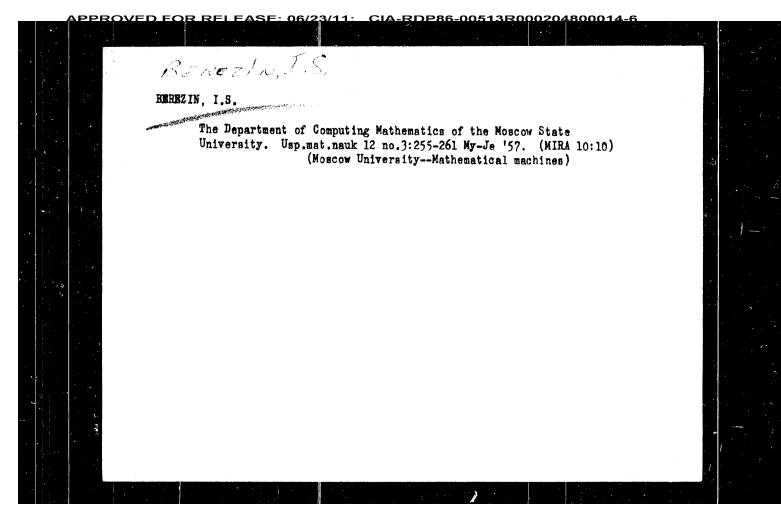
Metody vychisleniy, t. 1 (Calculation Methods, Vol. 1) Moscow, Fizmatgiz, 1959. 464 p. 20,000 copies printed.

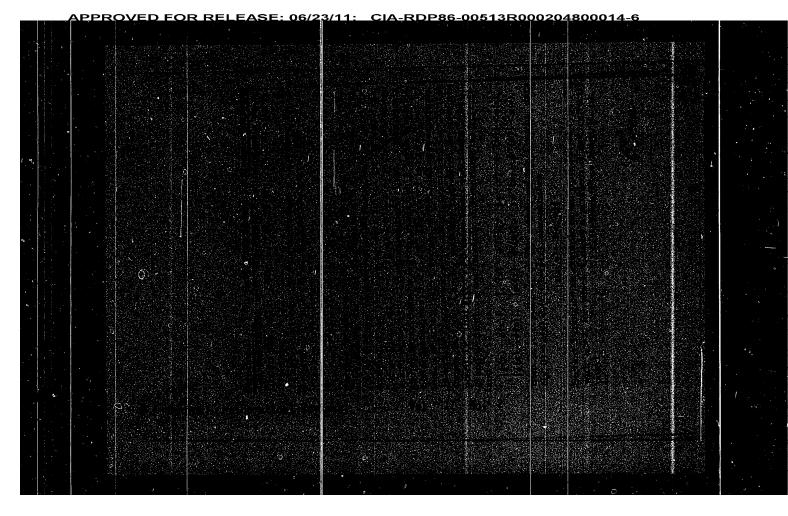
Eds.: B. M. Budak and A. D. Gordunov.

FURPOSE: This textbook is intended for students of mechanics and mathematics specializing in computational mathematics. It will be of interest to students of the theory and practice of numerical methods.

COVERAGE: This is the first of a 2-volume work based on courses given in the Department of Mechanics and Mathematics at Moscow State University. The book discusses operations with approximate numbers, the interpolation theory, numerical differentiation, numerical integration, and uniform and meansquare approximations of functions. The authors thank Academician S.L. Sobolev, Corresponding Member of the Academy of Sciences, USSR; Professor L. A. Lyusternik, Professor A. A. Lyapunov; Professor M. R. Shure-Bure; Docent A. D. Gorbunov; V. G. Kermanov; V. V. Rusanov; Yu. A. Shreyder; and

Card its





EEREZIN, I. S.

"The Gauchy Problem for Equations of the Hyperbolic Type With Initial Given Quantities on the Parabolicity Line." Sub 23 Apr 47, Moscow Order of Lenin State U imen! M. V. Lomonosov

Dissertations presented for degrees in science and engineering in Moscow in 1947

SO: Sum No. 457, 18 Apr 55

PANASEVICH, M.A.; EEREZIN, I.P., kand. med. nsuk

Case report on extrauterine pregnancy. Akush. i gin. 39 no.3:
132 My-1e¹63

1. Iz ginekologicheskogo otdeleniya (zav. M.A. Panasevich)
58-y gorodskoy bol'nitsy (glavnyy vrach S.G. Rynkevich) Moskvy.

中特力 ACC NR: AP6031639 condition in the tissues. The following coefficients were used to analyze the results: K_1 represented the relationship of the maximal force of the current to the original force and also the degree of disturbance of the tissue after oxygenic stress. K_2 , K_3 , and K_4 represented the relation of the current forces at 60, 120, and 180 seconds after the first supply of oxygen. Analysis of the data showed that a single inoculation of DNPH produces a significant reduction in the saturation of oxygen in muscles, and increases oxygen consumption. In addition, a more severe experiment was conducted by applying arterial gaskets to the limbs and then inoculating DNPH. Analysis of this method also showed that a single inoculation of DNPH produces a significant increase (43%) in 02 consumption. It was concluded that the electroanalytic method permits correlation of respiratory intensity in intact muscles of living organisms and expression of respiratory kinetics by a constant of reaction speed. This method of registering $\mathbf{0}_2$ consumption in living tissues can also be used in tracing the effect of a small dose of DNPH over a long period of time. [WA-50; CBE No. 12] SUB CODE: 06 / SUBM DATE: 07.Jan66 / ORIG REF: 010 / OTH REF: 002

SOURCE CODE: UR/0240/66/000/009/0067/0071 AUTHOR: Popov, T. A.; Epshteyn, L. M.; Berczin, I. P.
ORG: Institute of General and Municipal Hygiene im. A. N. Sysin, AMN SSSR ACC NR. AP6031639 (Institut obshchey i kommunal noy gigiyony AMN SSSR); State Institute of Oncology im. I. A. Gertsen (Gosudarstvennyy onkologicheskiy institut); Institute of Experimental and Surgical Apparatus and Instruments, Moscow (Institut eksperimental'noy TITIE: Electroanalytic method of studying the speed of oxygen consumption in tissues in vivo in a sanitary-toxicological experiment TOPIC TAGS: electroanalysis, exygen consumption, rat, histology, toxicology The electroanalytic method of studying $p0_2$ in the tissues of ABSTRACT: a living organism has been proven to be a sensitive test affiliated with the determination of the MPC (maximum permissible concentration) of a series of tissues. Experiments were conducted with white rats: in one group, a water solution of 2,4 dinitrophenol (DNPH) with a concentration of 1/2 LD₅₀ (1.5 mg/kg) was injected in the course of 80 days; in the second group the same dosage of DNPH was injected once; the third group was the control and received no injection. A specially constructed organic glass chamber which supplied 100% oxygen at a rate of 5 %/min, thus allowing a full exchange of the air with respired CO2, was used. An electronic self-recording potentiometer (YePP09) studied the oxygenic UDC: 615.9:614.37-092-07:616-008.922.1-074 Card 1/2

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L 11375-67

ACC NR: AT6036498

after cut-off of oxygen breathed for 30 min at pressures of 1, 2, 3, and 3.6 at.

The 5th series was conducted at 3 at. but with CO₂ removed from the respiratory tract after external respiration with oxygen was cut off; the 6th series was designed to show the effect of CO₂ on tissue O₂ saturation at 3 at. and the 7th series studied the persistence of brain bioelectric activity when circulation and respiration cease simultaneously.

It was found that brain bioelectric activity in rabbits always persists considerably longer under conditions of pressure oxygen breathing than at normal pressure, and that up to a certain point the persistence of EEG activity increases with increased atmospheric pressures.

The experimental data obtained show that respiration of atmospheres with elevated pO₂ creates considerable oxygen reserves in the tissues, which may serve both therapeutic as well as other medical and biological purposes. [W.A. No. 22; ATD Report 66-116]

SUB CODE: 06 / SUBM DATE: OCMay66

Card 2/2 egk

L 11375-67 ACC NR: AT6036498

SOURCE CODE: UR/0000/66/000/000/0065/0066

AUTHOR: Berezin, I. P.; Seregin, G. I.; Rostovtsev, B. N.

ORG: none

TITLE: Experimental evidence of the establishment of an oxygen reserve during oxygenation of tissues under high pressure Paper presented at the Conference on Problems of Space Medicine held in Moscow from 24 to 27 May 1966]

SOURCE: Konferentsiya po problemam kosmicheskoy meditsiny, 1966. Problemy kosmicheskoy meditsiny. (Problems of space medicine); materialy konferentsii, Moscow, 1966, 65-66

TOPIC TAGS: hyperoxia, oxygen excess pressure, electroencephalography, animal physiology, tissue oxygen saturation

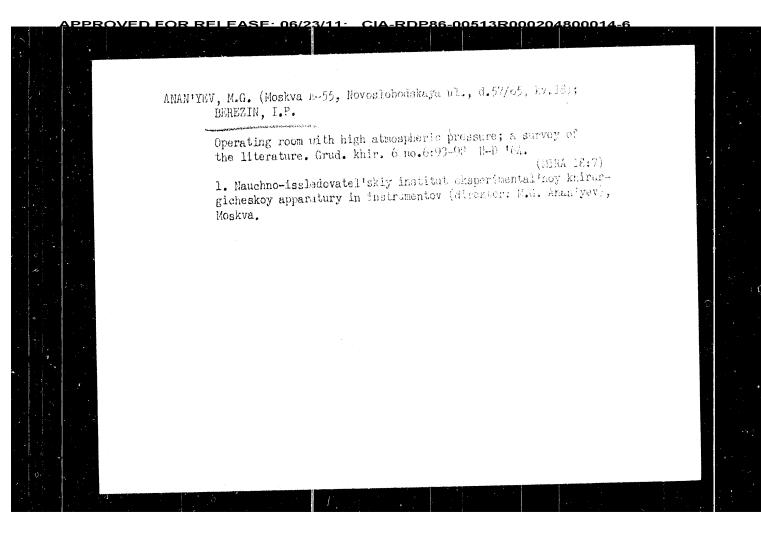
ABSTRACT: Because existing procedures for theoretical computation of the oxygen reserves created in the organism by excess pressure oxygen breathing are difficult and sometimes imprecise, studies were conducted to determine experimentally the degree of oxygen reserves created in the animal organism under various definite conditions. The duration of continued EEG activity in the brain of rabbits after the cessation of respiration was used as an index of the oxygen reserve. Altogether, 7 series of experiments were conducted on 70 rabbits in an experimental pressurized operating room: the first 4 series studied the duration of continued brain bioelectric activity

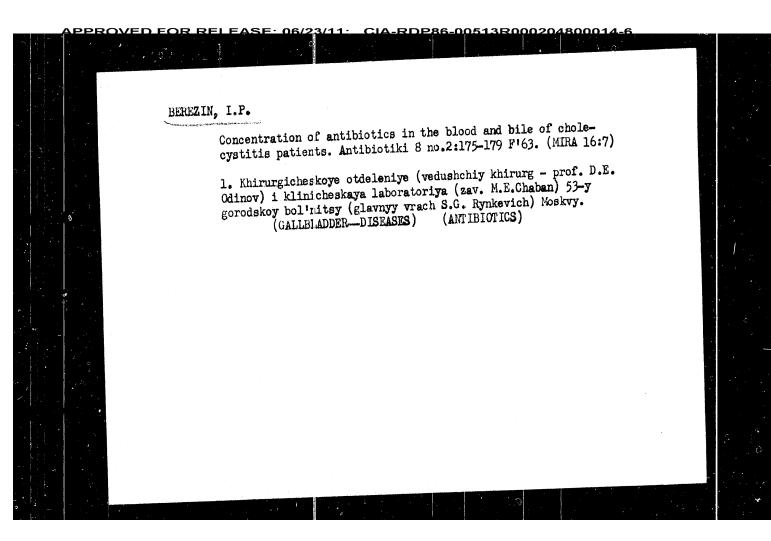
BEREZIN, I.P.; EPSHTEYN, I.M.; KASHCHEVSKAYA, L.A.

Use a pair of gold and iron electrodes in electrochemical registration of the oxygen regime in tissues in vivo. Eksper. khir. i anest. 9 no.3:18-19 My-Je '64. (MIRA 18:3)

1. Nauchno-isslelovatel'skiy institut eksperimental'nov khirurgicheskoy apparatury i instrumentov (dir. N.G. Aman'yev) i Onkologicheskiy institut imeni Gertsena (dir. - prof. A.N. Novikova), Moskva.

ANAN'YEV, M.G.; BEREZIN, I.P.; SHCHUPAKOV, N.N.; KOPYLOV, V.I. Surgery performed in an operating room under increased atmospheric pressure. Eksper. khir. i anest. 9 no.3:14-18 My-Je '64. (MIRA 18:3) 1. Nauchno-issledovatel'skiy institut eksperimental'noy khirurgicheskoy apparatury i instrumentov (dir. M.G. Anan'yev) i Vsesoyuznyy tsentral'nyy nauchno-issledovatel'skiy institut okhrany truda (dir. M.Ye. TSutskov) Vsesoyuznogo tsentral'nogo soveta professional'nykh soyuzov, Moskva.





DEREZIN, I. P. (Moskva, K-9, Stoleshnikov per., 5, kv. 36);
GULGSUVSKAYA, M. A. (Moskva, Leninskiy pr., 7, kv. 20)

Cystoadenoma of the pancreas. Vop. onk. 6 no. 12:57-59 '60.
(MIRA 15:7)

1. Iz khirurgicheskogo otdeleniya (vedushchiy khirurg - prof.
D. S. Odinov), patologoanatomicheskogo otdeleniya (zav. otdeleniyem - prof. I. A. Kusavitskiy) 53-y Moskovskoy gorodskoy bol'nitsy (glavnyy vrach - S. G. Rynkevich).

(PANCREAS--TUMORS)